

THE APPLICATION OF  
NONEQUILIBRIUM THERMODYNAMICS

by

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TABLE OF CONTENTS

	Page
CHAPTER 1. INTRODUCTION . . . . .	1
1. Foreword . . . . .	1
2. On Irreversibility . . . . .	2
3. Historical Development . . . . .	3
4. Onsager's Reciprocal Relations . . . . .	4
5. Significance of Thermodynamic State Functions in Nonequilibrium States. . . . .	7
CHAPTER 2. ON THE APPLICATION OF ONSAGER'S RECIPROCAL RELATIONS . . . . .	10
CHAPTER 3. ISOTHERMAL MULTICOMPONENT DIFFUSION. . . . .	15
1. Introduction . . . . .	15
2. Diffusional Phenomena. . . . .	16
3. Frames of Reference. . . . .	17
4. Relationships Among Fluxes Based on Various Frames of Reference. . . . .	20
5. Legitimate Choice of Conjugated Forces and Fluxes. . . . .	22
6. Gradient of Chemical Potential as Driving Forces . . . . .	23
7. Summary. . . . .	28
CHAPTER 4. A FORMALISM DUE TO TYKODI AND ITS APPLICATIONS . . . . .	29
1. Introduction . . . . .	29
2. Basic Technique. . . . .	29
3. Thermodynamic Relations. . . . .	32
4. Migrational Equilibrium. . . . .	35

5. Migrational Equilibrium in a Monothermal Concentration Field. . . . .	37
6. A General Problem of Migrational Equilibrium . . .	41
7. Correction for Manometer Readings. . . . .	44
8. Mass Transfer Processes. . . . .	47
9. Summary. . . . .	49
ACKNOWLEDGEMENT. . . . .	50
BIBLIOGRAPHY . . . . .	51
NOMENCLATURE . . . . .	53

## Chapter 1

### INTRODUCTION

1. Foreward: It is often maintained that thermodynamics is concerned with reversible processes and equilibrium states, and that problems associated with irreversibility lie outside its scope. Starting with three fundamental postulates and a number of state functions defined for the equilibrium states, the classical equilibrium thermodynamics has developed into a most satisfactory axiomatic science. Another aspect of the equilibrium thermodynamics is its phenomenological attitude. With its foundation seated on a basis free from any considerations of the structure of matter, the equilibrium thermodynamics has yielded important results entirely unshaken by the quantum revolution. There arises the question of the feasibility of the extension of the methods of equilibrium thermodynamics into the realm of non-equilibrium (or irreversible) phenomena. A phenomenological theory of irreversible processes should aspire to encompass within a simple scheme a wide range of non-equilibrium phenomena. Like other macroscopic disciplines, such as fluid mechanics and electromagnetism, the thermodynamics of irreversible processes should be based on a scheme of continuum field with characteristic continuous functions of space coordinates and time. In contrast to the classical equilibrium thermodynamics, in which the state variables are usually independent of the space coordinates, the thermodynamics of irreversible processes should have its formulation in the forms of local equations just as in fluid

dynamics and the Maxwellian theory of electromagnetism.

2. On Irreversibility: There are two erroneous criteria popularly considered to be characteristic of irreversibility, namely spontaneous occurrence of a process, and the running of the process at a finite rate. Bridgman (1) has indicated that a finite and reversible flow of heat could be maintained by the action of a thermo-motive force (in analogy with the electro-motive force of electrodynamics). The increase of entropy is the ultimate criterion of irreversibility. There are probably other criteria of less general scope. An explicit criteria for irreversibility suggests itself when the differential equations describing some time-dependent physical processes are examined. If those equations are invariant with regard to the algebraic sign affixed to the variable time, the process is considered as reversible, otherwise it is called irreversible. As an example, the wave equation which describes the propagation of waves in a non-absorbing medium is (2):

$$\frac{1}{c^2} \frac{\partial^2 U}{\partial t^2} = \frac{\partial^2 U}{\partial x^2} + \frac{\partial^2 U}{\partial y^2} + \frac{\partial^2 U}{\partial z^2} \quad (1-1)$$

It is seen that this equation is invariant for the substitution of  $t$  by  $-t$  and the propagation, which is of natural occurrence and takes place at a finite rate, is a reversible process.

On the other hand, the transport equation which characterizes the usual physical processes of diffusion and conduction of heat, etc.,

$$\frac{1}{c^2} \frac{\partial T}{\partial t} = \frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} \quad (1-2)$$

is not invariant with respect to such a substitution and it describes an irreversible process, or more exactly, the irreversible approach to equilibrium.

3. Historical Development: There began to appear in the middle of the nineteenth century scattered treatments on irreversible processes. The study on the action of thermocouple by W. Thomson, Lord Kelvin (3) was probably the first case known in the scientific literature. Lord Kelvin succeeded in correctly deriving two relations by resorting to an altogether intuitive and unjustifiable inference, known as Kelvin's Hypothesis. In the action of thermocouple there are two irreversible processes accompanying the thermoelectric process, namely thermal conduction and the development of Joulean heat. Kelvin postulated that reversible processes were separable from irreversible processes in the sense that thermodynamics could be applied to reversible processes as if the accompanying irreversible processes were absent. In Kelvin's work, the thermoelectric phenomena was taken as the reversible process to which application of thermodynamics was directed. It may be cited that Boltzmann (4) attempted without success to justify Kelvin's Hypothesis.

It was not until 1931 when Onsager (5) proposed the "reciprocal relations" that the treatments of irreversible phenomena were founded on a rational scheme. Later on Meixner (6) and somewhat later Prigogine (7) succeeded in establishing a

consistent phenomenological theory of the irreversible processes, incorporating both Onsager's reciprocal relations and a scheme for explicit calculation of the so-called entropy source strength in a certain number of physical situations. In this direction a unified front was rapidly developed in the last two decades.

4. Onsager's Reciprocal Relations: In its original form, the context of Onsager's theory (5) may be stated as follows:

When a set of  $n$  thermodynamic fluxes  $J_i$  are linearly related to  $n$  thermodynamical forces  $X_i$ :

$$J_i = \sum_{j=1}^n L_{ij} X_j, \quad i = 1, 2, \dots, n, \quad (1-3)$$

and if each flux is the time derivative of a thermodynamic variable  $a_i$ :

$$J_i = \dot{a}_i \quad (1-4)$$

while each  $a_i$  is an even function of the particle velocities (for instance, local energies, concentrations, etc. which are not affected by the sense or direction of velocity vectors), and the entropy of the system could be approximated by:

$$S = \frac{1}{2} \sum_{i=1}^n \sum_{j=1}^n g_{ij} a_i a_j, \quad (1-5)$$

and the forces  $x_j$  have been chosen so that:

$$x_j = \left( \frac{\partial S}{\partial a_j} \right) = \sum_{i=1}^n g_{ij} a_i \quad (1-6)$$

then, the matrix  $L_{ij}$  of the phenomenological coefficients  $L_{ij}$  in Equation (1-3) is symmetric; i.e.,

$$L_{ij} = L_{ji} \quad (1-7)$$

The modification required in the general case (when the  $a_i$  can be odd functions of the particle velocities, e.g., momentum densities) were given by Casimier (8).

Under certain circumstances the matrix  $L_{ij}$  is not symmetric. When an external magnetic field acts on the system, the reciprocal relations become:

$$L_{ij}(B) = L_{ji}(-B) \quad (1-8)$$

where  $B$  is the magnetic induction. Thus,  $L_{ij}$  is the same function of  $B$  as  $L_{ji}$  is of  $-B$ .

A similar relation holds for the situation in which the Coriolis forces are present, i.e., when the system is in rotation. The reciprocal relations in this case are:

$$L_{ij}(\omega) = L_{ji}(-\omega) \quad (1-9)$$

where  $\omega$  is the angular velocity of rotation.

Some elaboration on Equation (1-5) will probably clarify the approximations involved. When the entropy,  $S$ , of a system is considered as a function of thermodynamic variables  $a_i$ :



$$S = S(a_1, a_2, \dots, a_n) \quad (1-10)$$

where all the quantities represent the deviations from their equilibrium values,  $S^0$  and  $a_i^0$ ,  $i = 1, 2, \dots, n$ .

Taylor series expansion of  $S$  around  $a_i^0$  leads to

$$S = \sum_{i=1}^n \left( \frac{\partial S}{\partial a_i} \right)_{a_i=0} a_i + \frac{1}{2} \sum_{i=1}^n \sum_{j=1}^n \left( \frac{\partial^2 S}{\partial a_i \partial a_j} \right)_{a_i=0, a_j=0} a_i a_j + \dots \quad (1-11)$$

where terms of degree higher than the second are neglected. Since the entropy of the system assumes the maximum value at equilibrium condition, the first term of the right hand side of Equation (1-11) vanishes, and Equation (1-11) is reduced to Equation (1-5)

$$S = \frac{1}{2} \sum_{i=1}^n \sum_{j=1}^n g_{ij} a_i a_j, \quad (1-5)$$

where

$$g_{ij} = \left( \frac{\partial^2 S}{\partial a_i \partial a_j} \right)_{a_i=0, a_j=0}$$

An important theory connected with the application of Onsager's method will be stated. Equation (1-3) represents a mathematical statement of the physical phenomena to be called "coupling" hereafter. Two rate processes are said to be coupled

when the force of one of them induces flux of another. Thus a temperature gradient is known to cause diffusion of matter (Soret effect) and on the other hand a concentration gradient tends to induce heat flow (Dufour effect). Equation (1-3) describes the flux of a certain kind (heat or material of certain components) in terms of linear combinations of all the "forces" present in the system. The coefficients  $L_{ij}$  characterize the coupling effect. The vanishing of a coefficient  $L_{ij}$  indicates the absence of coupling effect between two phenomena. There is a rule known as the Curie's theorem (9) which offers a definite answer as to the occurrence of coupling between two phenomena. Curie's theorem states that entities whose tensorial characters differ by an odd integer cannot interact in an isotropic media. Some physical processes are often classified according to their tensorial character. The tensorial character of a process is determined by tensorial rank of its force. Under the category of the scalar phenomena (tensor of rank one) there are chemical reactions and structure relaxation. The vectorial processes (tensor of rank two) include diffusion, heat conduction, etc. Viscous phenomena is an example of the tensorial (tensor of rank three) processes.

In practice, however, the coupling effect between phenomena of different tensorial ranks is always negligibly small. Consequently, only coupling among processes with equal tensorial ranks needs to be considered.

5. Significance of Thermodynamic State Functions in Non-equilibrium States: The thermodynamics of irreversible processes

aims at extending the method and scope of the classical equilibrium thermodynamics. All the thermodynamical state functions (such as temperature, entropy, etc.) which are strictly defined for equilibrium states are to be used in the description of non-equilibrium phenomena. This rather contradictory attitude may be justified when the treatments are confined to phenomena which are not far removed from equilibrium states. In this conjunction, a postulate which may be named the postulate of local equilibrium (9) will have to be introduced. This may be stated as follows: for a system in which irreversible processes are taking place, all thermodynamic functions of state exist for each element of the system. These thermodynamic quantities for the non-equilibrium system are the same functions of the local state variables as the corresponding equilibrium thermodynamic quantities. The validity of this postulate has been investigated by Prigogine (10) from a microscopic viewpoint. In the Chapman-Enskog (11) theory, the molecular distribution function is expressed in an infinite series

$$f = f_0 + f_1 + f_2 + \dots \quad (1-12)$$

where  $f_0$  is the equilibrium molecular distribution function,  $f_1$  is the first-order corrections, and  $f_2$ , etc., are subsequent corrections. For a system which is close to the equilibrium, the successive corrections  $f_1$ ,  $f_2$ , etc. become smaller and smaller. Prigogine (10) has established that the usual thermodynamic quantities defined for the equilibrium conditions retain their significance when the molecular distribution functions can

be characterized by  $f = f_0 + f_1$ . Prigogine's analysis was based on mixtures of monoatomic gases and dependent on the Chapman-Enskog model. In general, the domain of validity of the postulate of local equilibrium is still not established.

## Chapter 2

## ON THE APPLICATION OF ONSAGER'S RECIPROCAL RELATIONS

There is a widespread misunderstanding concerning the choice of fluxes and forces in conjunction with the use of the Onsager reciprocal relationships. For the sake of convenience, the context of Onsager's relations, as stated in Chapter 1, will be reproduced here.

When a set of  $n$  "thermodynamical fluxes"  $J_i$  are linearly related to " $n$  thermodynamical forces"  $X_i$ :

$$J_i = \sum_{j=1}^n L_{ij} X_j, \quad i = 1, 2, \dots, n \quad (2-1)$$

and if each flux is the time derivative of a thermodynamic variable  $a_i$ :

$$J_i = \dot{a}_i, \quad (2-2)$$

while each  $a_i$  is an even function of the particle velocities and the entropy of the system could be approximated by:

$$S = \frac{1}{2} \sum_{i=1}^n \sum_{j=1}^n g_{ij} a_i a_j, \quad (2-3)$$

and if the forces  $X_j$  have been chosen so that:.

$$X_j = \left( \frac{\partial S}{\partial a_j} \right) = \sum_{i=1}^n g_{ij} a_i, \quad (2-4)$$

then, the Matrix  $L_{ij}$  of the phenomenological coefficients  $L_{ij}$  in Equation (2-1) is symmetric; i.e.,

$$L_{ij} = L_{ji} \quad (2-5)$$

A celebrated equation relating the entropy production to the "forces" and "fluxes",

$$\dot{S} = \sum_{i=1}^n X_i J_i \quad (2-6)$$

may be obtained as follows. One differentiates Equation (2-3) with respect to time to obtain

$$\dot{S} = \sum_{i=1}^n \sum_{j=1}^n g_{ij} \dot{a}_i a_j \quad (2-7)$$

On comparing this expression with Equations (2-2) and (2-4), one sees that Equation (2-6) is a necessary consequence.

Although Equation (2-6) results from Equations (2-2) through (2-4), there is no assurance that the Onsager Reciprocal Relations as expressed in Equation (2-5) follow from Equations (2-1) and (2-6). In current literature (12), (13), one encounters many examples of indiscriminate choice of forces and fluxes based on the erroneous notion that Equations (2-1) and (2-6) establish Onsager's Reciprocal Relations. Coleman and Truesdell (14) have demonstrated that a set of conjugated forces and fluxes satisfying Equations (2-1) and (2-6) may not fulfill the requirement of Onsager's Reciprocal Relations. In the following, a brief proof essentially after Coleman and Truesdell will be given. Based on a set of conjugated fluxes,  $J_i$  and forces,  $X_i$  which obey Equations (2-1), (2-6), and (2-5), one can construct in an infinite number of ways new sets of fluxes and

forces satisfying Equations (2-1) and (2-6):

$$J_i' = \sum_{j=1}^n L_{ij}' X_j' \quad (2-1')$$

$$\sum_{i=1}^n X_i' J_i' = \sum_{i=1}^n X_i J_i = \dot{S} \quad (2-6')$$

but yielding nonsymmetric matrices  $[L_{ij}']$  of the phenomenological coefficients  $L_{ij}'$ . To be specific, let  $[W_{ij}]$  be any nonzero  $n \times n$  skew matrix; i.e., let the components of  $[W_{ij}]$  be such that for all the pairs of  $i, j$ :

$$\begin{aligned} W_{ij} &= -W_{ji}; \quad i = 1, 2, \dots, N \\ j &= 1, 2, \dots, N \end{aligned} \quad (2-8)$$

and, for at least one such pair with  $j \neq i$ , let  $W_{ij} \neq 0$ .

Consider the set of fluxes  $J_i'$  and forces  $X_i'$  defined as follows:

$$J_i' = J_i + \sum_{j=1}^n W_{ij} X_j \quad (2-9)$$

$$X_i' = X_i \quad (2-10)$$

for all  $i, j$ . Then:

$$\sum_{i=1}^n J_i' X_i' = \sum_{i=1}^n J_i X_i + \sum_{i=1}^n \sum_{j=1}^n W_{ij} X_j X_i \quad (2-11)$$

That the second term of the right side of the above equation vanishes is a consequence of Equation (2-8). Hence, it follows that:

$$\sum_{i=1}^n J_i' X_i' = \sum_{i=1}^n J_i X_i = \dot{S} \quad (2-12)$$

Now, from Equations (2-1), (2-9), and (2-10), there results:

$$J_i' = \sum_{j=1}^n L_{ij} X_j + \sum_{j=1}^n W_{ij} X_j = \sum_{j=1}^n (L_{ij} + W_{ij}) X_j' \quad (2-13)$$

and one obtains, by comparing Equation (2-13) with Equation (2-1')

$$L_{ij}' = L_{ij} + W_{ij} \quad (2-14)$$

or

$$[L_{ij}'] = [L_{ij}] + [W_{ij}] \quad (2-15)$$

Therefore,  $L_{ij}'$ , being the sum of a symmetric matrix  $L_{ij}$  and a nonzero skew matrix  $W_{ij}$ , is nonsymmetric.

Most of the current treatments (4), (12), (13), on the application of Onsager's theory rely on Equation (2-6) in the choice of conjugated forces and fluxes.

It has been recognized that phenomenological theories of various kinds easily yield a relation of the type Equation (2-6) while relations of the type exemplified in Equations (2-2) through (2-4) are more difficult to establish. Therefore, if one



takes Equations (2-1) through (2-4) as the hypothesis of Onsager's theorem, then the choice of the fluxes and forces is greatly limited. Of course, it is possible that some other choice of fluxes might also lead to Equation (2-5). But, until the forces and fluxes in any particular case are physically identified by some property more specific than their mere entry into the bilinear form of Equation (2-6), application of Onsager's theorem is precarious.

## Chapter 3

## ISOTHERMAL MULTICOMPONENT DIFFUSION

1. Introduction: The main context of the previous chapter was to demonstrate that the legitimate choice of conjugated forces and fluxes in connection with Onsager's Reciprocal Relations rests upon a more fundamental criterion than the invariance of entropy production. Use of the set of original conditions as expressed by Equations (2-2) through (2-4) entails a detailed knowledge of microscopic nature and will defy the spirit of phenomenological approach. From a phenomenological point of view, the correct choice of conjugated forces and fluxes relies solely upon experimental investigations. A comprehensive experimental research in an attempt to examine the validity of Onsager's Reciprocal Relations has been carried out recently by D. G. Miller (13). In his experimental investigation Miller selected the conjugated forces and fluxes on the basis of the invariance of entropy production. As was pointed out in Chapter 2, the criterion of the invariance of entropy production as expressed in Equation (2-6) is an erroneous one. In this light one may look at Miller's work as a search for legitimate choices of conjugated forces and fluxes rather than a direct attempt at the verification of the Onsager's Reciprocal Relations.

Apart from the proposition of Onsager's Reciprocal Relations, the thermodynamics of irreversible processes aims at establishing the true "forces" behind the processes. The correct

choice of conjugated forces and fluxes is itself a major task in the application of irreversible thermodynamics.

2. Diffusional Phenomena: In diffusional phenomena, the classical Fick's law attributes the cause of diffusion to the concentration gradient. The diffusional coefficients thus defined are found to depend on the concentration and, hence, are not true constants. In the formulation of irreversible thermodynamics the flux is written as linear combination of certain forces (as in Equation (2-1)):

$$J_i = \sum_{j=1}^n L_{ij} X_j \quad (2-1)$$

where the  $L_{ij}$ 's are true coefficients in the sense that they are independent of the forces. For isothermal diffusion it has been proposed that the gradient of chemical potential is the true cause of diffusion (12), (13). Thus, for an n-component system under isothermal condition, one may write:

$$J_i = \sum_{j=1}^n L_{ij} \nabla \mu_j, \quad i = 1, 2, \dots, n \quad (3-1)$$

where  $\nabla \mu_j$  denotes the chemical potential of component j.

The present chapter is concerned with the question of the real force in the diffusional processes. If the diffusional coefficients defined in terms of Equation (1) prove to be true constants, the gradient of chemical potential should be considered as the real cause of diffusional phenomena, and Equation (3-1) should be preferred to Fick's law. Besides, the Onsager

## Reciprocal Relations:

$$L_{ij} = L_{ji} \quad (2-5)$$

could be used with benefit to reduce the experimental work in determining diffusional coefficients.

Isothermal diffusional processes are described mathematically by flow equations in which the flux or current,  $J_i$  of the component  $i$  is expressed as a linear combination of pertinent forces. In experimental work the flux  $J_i$  of the component  $i$  is equated to the sum of concentration gradients each multiplied by a diffusion coefficient  $D_{ij}$  of one type. In the formalism of irreversible thermodynamics the flux  $J_i$  of the component  $i$  is expressed as the sum of the gradient of chemical potential of each component multiplied by a diffusion coefficient  $i_j$  of another type. In the following the  $D_{ij}$  will be referred to as practical diffusion coefficients and the  $i_j$  as fundamental diffusion coefficients. Since the flux  $J_i$  may be defined in various ways by choosing different frames of reference, the values of both practical and fundamental coefficients depend on the frame of reference selected. Following Fujita (15) and Kirkwood, et al. (16), one identifies four different types of frames of reference capable of clear definition. In the definitions of the various reference frames, one dimensional diffusion will be considered.

3. Frames of Reference: In defining the cell-fixed frame, one visualizes a cross-sectional plane  $1 \text{ cm}^2$  in area and perpendicular to and fixed with respect to the wall of the cell.

The flux  $(J_i)_c$  of component  $i$  is defined as the number of grams of  $i$  crossing the mentioned plane in one second. If the mean linear velocity of the component  $i$  with respect to the cell is denoted by  $(U_i)_c$  and the concentration in gram per cc by  $C_i$ , it follows from the definition that:

$$(J_i)_c = (U_i)_c C_i \quad (3-2)$$

One may choose as the reference plane a plane moving with the mean velocity  $(U_0)_c$  of the solvent. The subscript 0 will be used to represent the solvent hereafter. The flux  $(J_i)_0$  of component  $i$  on this solvent-fixed frame is related to  $(J_i)_c$  as follows:

$$(J_i)_0 = (J_i)_c - (U_0)_c C_i \quad (3-3)$$

By substituting  $i = 0$  into Equation (3-3) and noting that

$(J_0)_0 = 0$ , one obtains:

$$(U_0)_c = (J_0)_c / C_0, \quad (3-4)$$

and Equation (3) takes the form:

$$(J_i)_0 = (J_i)_c - (C_i / C_0) (J_0)_c \quad (3-5)$$

The velocity of the center of mass relative to the cell is defined as:

$$(U)_{MC} = \frac{\sum_{i=0}^{n-1} C_i (U_i)_c}{\sum_{i=0}^{n-1} C_i} \quad (3-6)$$

Making use of Equation (3-2) and the expression for the density of the system  $\rho = \sum_{i=0}^{n-1} C_i$ , one rewrites Equation (3-6) in the following form:

$$(U)_{MC} = \left(\frac{1}{\rho}\right) \sum_{i=0}^{n-1} (J_i)_C \quad (3-7)$$

One now defines a plane moving with the velocity  $(U)_{MC}$  as the mass-centered frame. The flux  $(J_i)_M$ , of component  $i$  based on the mass-centered frame is then written as:

$$(J_i)_M = (J_i)_C - (U)_{MC} C_i \quad (3-8)$$

Or, substituting Equation (3-7) into Equation (3-8), one has

$$(J_i)_M = (J_i)_C - (C_i/\rho) \sum_{i=0}^{n-1} (J_i)_C \quad (3-9)$$

Finally one may choose as the reference frame a plane moving with the volume-centered velocity  $(U)_{vc}$  which is defined as:

$$(U)_{vc} = \frac{\sum_{i=0}^{n-1} V_i C_i (U_i)_C}{\sum_{i=0}^{n-1} V_i C_i} \quad (3-10)$$

where  $\nabla_i^{C,C}/g$  denotes the partial specific volume of component  $i$ . Since:

$$\sum_{i=0}^{n-1} V_i C_i = 1, \quad (3-11)$$

Equation (3-11) can be rewritten as:

$$(U)_{VC} = \sum_{i=0}^{n-1} \nabla_i (J_i)_C, \quad (3-12)$$

and the flux,  $(J_i)_V$  of component  $i$  based on the volume fixed frame is in the form:

$$(J_i)_V = (J_i)_C - (U)_{VC} C_i = (J_i)_C - C_i \sum_{j=0}^{n-1} \nabla_j (J_j)_C \quad (3-13)$$

4. Relationships Among Fluxes Based on Various Frames of Reference: The relationships among the  $(J_i)_O$ ,  $(J_i)_M$ , and  $(J_i)_V$  may be derived by simple manipulations. For example, combining Equations (3-5), (3-11), and (3-13) one obtains:

$$(J_i)_V = (J_i)_O - C_i \sum_{j=1}^{n-1} \nabla_j (J_j)_O, \quad (J_0)_O = 0 \quad (3-14)$$

$$i = 1, 2, \dots, n-1$$

The flow equations based on the various frames of reference are now written as follows:

$$-(J_i)_O = \sum_{j=1}^{n-1} (D_{ij})_O C_j \quad i = 1, \dots, n-1 \quad (1-15)$$

$$-(J_i)_M = \sum_{j=1}^{n-1} (D_{ij})_M C_j \quad (1-16)$$

$$-(J_i)_V = \sum_{j=1}^{n-1} (D_{ij})_V C_j \quad (1-17)$$

Here the  $n(J_i)$  are linearly dependent, hence only  $(n-1)$  fluxes appear in the equation and the negative sign is adopted in

conformity with the convention that the positive direction of flux is along the direction of decreasing concentration. When Equations (3-15) and (3-17) are substituted into Equation (3-14), one obtains:

$$(D_{ij})_V = (D_{ij})_0 - c_i \sum_{k=1}^{n-1} \bar{V}_k (D_{kj})_0 \quad (3-18)$$

In Equation (3-18), the diffusion coefficients  $(D_{ik})_V$  are expressed in terms of the coefficients  $(D_{ik})_0$ . One now seeks to invert Equation (3-18) in order to have  $(D_{ij})_0$  expressed in terms of  $(D_{ij})_V$ . To this end, one multiplies Equation (18) by  $\bar{V}_i$  and sums over the variable  $i$ :

$$\sum_{i=1}^{n-1} \bar{V}_i (D_{ij})_V = \sum_{i=1}^{n-1} \bar{V}_i (D_{ij})_0 - \sum_{i=1}^{n-1} c_i \bar{V}_i \sum_{k=1}^{n-1} \bar{V}_k (D_{ik})_0 \quad (3-19)$$

Since one has from Equation (3-5):

$$\sum_{i=1}^{n-1} c_i \bar{V}_i = 1 - c_0 \bar{V}_0,$$

Equation (3-19) becomes:

$$\sum_{i=1}^{n-1} \bar{V}_i (D_{ij})_V = c_0 \bar{V}_0 \sum_{i=1}^{n-1} \bar{V}_i (D_{ik})_0,$$

or

$$\sum_{i=1}^{n-1} \bar{V}_i (D_{ik})_0 = \frac{1}{c_0 \bar{V}_0} \sum_{k=1}^{n-1} \bar{V}_k (D_{kj})_V \quad (3-20)$$



Replacing the dummy index  $k$  on the right hand side of Equations (18) and (20) by  $i$  and comparing the resulting equations one obtains the desired relationship:

$$(D_{ij})_0 = (D_{ij})_V + \frac{C_i}{C_0 V_0} \sum_{i=1}^{n-1} \bar{V}_i (D_{ij})_V \quad (3-21)$$

5. Legitimate Choice of Conjugated Forces and Fluxes: At this point the question arises as to which set of fluxes, when conjugated with the gradient of chemical potential, will give the desired or the legitimate choice. Since the invariance of entropy production cannot be relied on in the determination of the correct set, either experimental verification or theoretical investigation of microscopic nature will serve as the basis. Hooyman (17) has shown that at thermal and mechanical equilibrium the solvent-fixed frame  $(J_i)_0$  is the desired set of fluxes.

Now, among the various set of fluxes, the cell-fixed frame is the only one that will conveniently yield to practical measurement. However, it can be shown (15) than, when average values of partial specific volumes  $\bar{V}_i$  can be used with reasonable accuracy, the volume-centered frame coincides with the cell-fixed frame.

When one writes the flow equation in its fundamental form based on the solvent-fixed frame of reference:

$$-(J_i)_0 = \sum_{j=1}^{n-1} (\Omega_{ij})_0 \nabla_j \mu, \quad i = 1, 2, \dots, n-1 \quad (3-22)$$

The resulting  $(\Omega_{ij})_0$  are the coefficients expected to obey Onsager's Reciprocal Relations. Moreover, Equation (3-22) would be considered as the fundamental flow equation giving account of the real "driving force".

6. Gradients of Chemical Potential as Driving Forces: It is the specific purpose of this chapter to examine the coefficients  $(\Omega_{ij})_0$  in Equation (3-22). Previous investigations (13) have been confined to the validity of Onsager's relations among the  $(\Omega_{ij})_0$  for  $i \neq j$ . No attention has thus far been paid to the dependency of  $(\Omega_{ij})_0$  on the chemical potential. From the practical point of view, the dependency of  $(\Omega_{ij})_0$  on the chemical potential is a more important problem than Onsager's Reciprocal Relations governing the cross coefficients  $(\Omega_{ij})_0$  for  $i \neq j$ , which are of less significance than the main coefficients  $(\Omega_{ij})_0$ . If the  $(\Omega_{ij})_0$  are found to be independent of the chemical potential, Equation (22) should replace Fick's law as the fundamental equation of diffusion.

Expressions for the  $(\Omega_{ij})_0$  in terms of the measurable  $(D_{ij})_0$  are derived as follows. One first rewrites Equation (22) by expressing  $\mu_j$  in terms of the gradients of concentration as:

$$-(J_i)_0 = \sum_{k=1}^{n-1} \sum_{j=1}^{n-1} (\Omega_{ij})_0 \frac{\partial \mu_j}{\partial C_k} \nabla C_k \quad (3-23)$$

Replacing the dummy index  $j$  in Equation (3-15) by  $k$  and comparing the resulting expression with Equation (3-23) one obtains:

$$(D_{ik})_0 = \sum_{j=1}^{n-1} (\Omega_{ij})_0 \frac{\partial \mu_j}{\partial c_k}, \quad i = 1, 2, \dots, n-1 \quad (3-24)$$

The inverted equations are:

$$(\Omega_{ij})_0 = \sum_{k=1}^{n-1} B_{jk} (D_{ik})_0, \quad i, j = 1, 2, \dots, n-1 \quad (3-25)$$

where  $B_{jk}$  are elements of the inverse matrix  $[B]$  of the matrix  $[\frac{\partial \mu}{\partial c}]$  in which  $\frac{\partial \mu_j}{\partial c_k}$  is an element of the  $j^{\text{th}}$  row and  $k^{\text{th}}$  column:

$$[B] = \left[ \frac{\partial \mu}{\partial c} \right]^{-1}$$

and

$$B_{jk} = \frac{\left| \frac{\partial \mu}{\partial c} \right|_{kj}}{\left| \frac{\partial \mu}{\partial c} \right|} \quad (3-26)$$

In Equation (3-26),  $\left| \frac{\partial \mu}{\partial c} \right|$  is the determinant of the matrix  $[\frac{\partial \mu}{\partial c}]$  and  $\left| \frac{\partial \mu}{\partial c} \right|_{kj}$  is the cofactor of the element  $\frac{\partial \mu_k}{\partial c_j}$ .

For three component system, Equation (3-25) takes the forms:

$$\begin{aligned} (\Omega_{11})_0 &= \frac{1}{\Delta} \left[ \frac{\partial \mu_2}{\partial c_2} (D_{11})_0 - \frac{\partial \mu_2}{\partial c_1} (D_{12})_0 \right], \\ (\Omega_{12})_0 &= \frac{1}{\Delta} \left[ \frac{\partial \mu_1}{\partial c_1} (D_{12})_0 - \frac{\partial \mu_1}{\partial c_2} (D_{11})_0 \right], \\ (\Omega_{21})_0 &= \frac{1}{\Delta} \left[ \frac{\partial \mu_2}{\partial c_2} (D_{21})_0 - \frac{\partial \mu_2}{\partial c_1} (D_{22})_0 \right], \end{aligned} \quad (3-27)$$

$$(\Omega_{22})_0 = \frac{1}{\Delta} \left[ \frac{\partial \mu_1}{\partial c_1} (D_{22})_0 - \frac{\partial \mu_1}{\partial c_2} (D_{21})_0 \right],$$

where

$$\Delta = \left( \frac{\partial \mu_1}{\partial c_1} \frac{\partial \mu_2}{\partial c_2} - \frac{\partial \mu_1}{\partial c_2} \frac{\partial \mu_2}{\partial c_1} \right)$$

The isothermal diffusion coefficients have been experimentally determined for some ternary systems. However, there is only one system, Na Cl - KCl - water at 25°C, for which complete thermodynamic data are available for direct computation of the  $(\Omega_{ij})_0$  from the  $(D_{ij})_0$ .

The data used in the following calculations are those summarized by Fitts (9).

For ternary systems, Equations (3-21) are in the form:

$$\begin{aligned} (D_{11})_0 &= (D_{11})_v + \frac{C_1}{C_0 \bar{V}_0} \left[ \bar{V}_1 (D_{11})_v + \bar{V}_2 (D_{21})_v \right] \\ (D_{12})_0 &= (D_{12})_v + \frac{C_1}{C_0 \bar{V}_0} \left[ \bar{V}_1 (D_{12})_v + \bar{V}_2 (D_{22})_v \right] \\ (D_{21})_0 &= (D_{21})_v + \frac{C_2}{C_0 \bar{V}_0} \left[ \bar{V}_1 (D_{11})_v + \bar{V}_2 (D_{21})_v \right] \\ (D_{22})_0 &= (D_{22})_v + \frac{C_2}{C_0 \bar{V}_0} \left[ \bar{V}_1 (D_{12})_v + \bar{V}_2 (D_{22})_v \right] \end{aligned} \quad (3-28)$$

Equations (3-27) and (3-28) are used to compute the  $(\Omega_{ij})_0$  from the data of Table 3-1. IBM-1620 was used for this, and the calculated results are presented in Table 3-2.

From the calculated results the following conclusions may

Table 3-1. Data for the system Na Cl - KCl - H<sub>2</sub>O at 25°C for four different compositions.\*

	A	B	C	D
$C_0(\text{g/cc})$	0.9855	0.9782	0.9808	0.9734
$C_1(\text{g/cc})$	0.01461	0.01461	0.02922	0.02922
$C_2(\text{g/cc})$	0.01863	0.03727	0.01863	0.03727
$V_0(\text{cc/g})$	1.002	1.002	1.0020	1.002
$V_1(\text{cc/g})$	0.3197	0.3270	0.3273	0.3339
$V_2(\text{cc/g})$	0.3872	0.3933	0.3941	0.4010
$(\frac{\partial \mu_1}{\partial c_1})/RT$	1.686	1.536	0.9502	0.8749
$(\frac{\partial \mu_1}{\partial c_2})/RT$	0.3791	0.2637	0.2628	0.2046
$(\frac{\partial \mu_2}{\partial c_1})/RT$	0.3745	0.2590	0.2579	0.1997
$(\frac{\partial \mu_2}{\partial c_2})/RT$	1.007	0.5586	0.9176	0.5129
$(D_{11})_v \times 10^5 \left(\frac{\text{cm}^2}{\text{sec}}\right)$	1.37	1.35	1.41	1.38
$(D_{12})_v \times 10^5 \left(\frac{\text{cm}^2}{\text{sec}}\right)$	-0.00	-0.00	-0.00	-0.00
$(D_{21})_v \times 10^5 \left(\frac{\text{cm}^2}{\text{sec}}\right)$	0.18	0.24	0.11	0.20
$(D_{22})_v \times 10^5 \left(\frac{\text{cm}^2}{\text{sec}}\right)$	1.82	1.83	1.81	1.83

\*The subscripts 0, 1, and 2 refer to H<sub>2</sub>O, Na Cl, and KCl respectively.

Table 3-2. Values of  $(\Omega_{ij})_0$  for the system Na Cl - KCl -  $H_2O$  at  $25^\circ C$  for four different compositions.

	A	B	C	D
$C_0(g/cc)$	0.9855	0.9782	0.9808	0.9734
$C_1(g/cc)$	0.01461	0.01461	0.02922	0.02922
$C_2(g/cc)$	0.01863	0.03727	0.01863	0.03727
$(\Omega_{11})_0 \times 10^5 : RT$	0.8890	0.9570	1.619	1.744
$(\Omega_{12})_0 \times 10^5 : RT$	-0.3243	-0.4325	-0.4406	-0.6531
$(\Omega_{21})_0 \times 10^5 : RT$	-0.3185	-0.4249	-0.4483	-0.5217
$(\Omega_{22})_0 \times 10^5 : RT$	1.940	3.525	2.115	4.323

be drawn. While the Onsager Reciprocal Relations:  $(\Omega_{12})_0 = (\Omega_{21})_0$ , are verifiable, the values of the  $(\Omega_{ij})_0$  are found to vary with the composition of the system. The significant fact is that the dependency of the  $(\Omega_{ij})_0$  on the composition is even more marked than that of the conventional Fick's law constants  $(D_{ij})_0$ . The unexpected results may be ascribed in part to the inaccuracy in the chemical potential data involved in the calculation. However, the variance of the so-called fundamental coefficients is so significant that there seems to be ample room for doubt as to the feasibility of replacing Fick's law by Equation (3-22) as the fundamental equation for diffusion.

7. Summary: The attempt to establish a fundamental equation for isothermal diffusion based on the scheme of irreversible thermodynamics has yielded negative results. As a by-product of this attempt, however, Onsager's Reciprocal Relations:  $(\Omega_{ij})_0 = (\Omega_{ji})_0$ , in this case, are found to hold reasonably well in agreement with Miller's work (13).

## Chapter 4

## A FORMALISM DUE TO TYKODI AND ITS APPLICATIONS

1. Introduction: In the present chapter a new approach developed by R. J. Tykodi is presented. The original treatises have appeared in a series of papers (18), (19) in the Journal of Chemical Physics. In dealing with non-equilibrium phenomena Tykodi's method aims at preserving the phenomenological spirit characteristic of the classical equilibrium thermodynamics. The physical quantities involved in this formalism are introduced in as operational a manner as possible. The scheme of presentation in this chapter will follow Tykodi's manuscript (20) of a forthcoming book. It is essential that the closed system approach is adopted to formulate a problem by Tykodi's method. In contrast to the open-system method which will usually provide a more clear cut approach to typical engineering problems, the closed-system method may tax the imagination more in defining a system. In formulating a problem the system is defined in such a way as to ensure that only heat and work can be exchanged between the system and the surroundings.

2. Basic Technique: The basic technique employed in analyzing a problem by Tykodi's approach is to define a system in such a way that the system may be separated into terminal parts and parts on-the-line (between terminal parts). The thermodynamic properties are uniform throughout each terminal part, and the gradients of the thermodynamic properties exist only in the parts on-the-line. The parts on-the-line are taken



to be point-wise time invariant. In this respect a severe restriction is imposed upon Tykodi's method. This approach is confined to the treatment of steady rate processes. In each case a definite amount of mass is taken as the system (See Fig. 1, with accompanying illustrations).

Four basic assumptions are made. They are:

1. The system is capable of sustaining steady-rate operations under the described conditions.

2. The system can always be divided into terminal parts and parts on-the-line, the parts on-the-line being stationary during steady-flow operations.

3. Certain non-flow states can be treated as being the limit of sequence of steady-flow operations.

4. In a sequence of steady-flow states converging on a non-flow state, the limiting state is a state of minimum entropy production relative to the neighboring flow states.

One may interpret the preceeding set of assumptions in the following manner. The first three assumptions are pure assumptions made on the physical situation. These three assumptions act together to impose an inherent limitation upon the scope of applicability of this method. The fourth assumption is of a rather different nature. It should be considered as a fundamental postulate upon which the validity of the whole scheme of Tykodi's approach is hinged. Tykodi has suggested (20) that the proof of assumption 4 may be obtained through statistical mechanical investigations. As a matter of fact, assumption 4 is known to hold in monothermal fields (i.e., the system is in

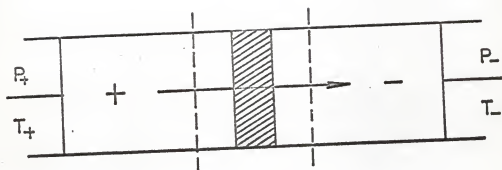


Fig. 1. A mass of gas in adiabatic flow across a porous plug,  $P_+ > P_-$ .

contact with a single heat reservoir) when the reference non-flow state is in a state of thermodynamic equilibrium; since the rate of entropy production is zero in a state of thermodynamic equilibrium, whereas, in any neighboring steady-flow state, the rate of entropy production must be positive definite.

Tykodi's theory of non-equilibrium phenomena may be said to be an exploration of the consequences of assumption 4 for general cases. In this chapter Tykodi's fourth assumption will be referred to as the fundamental postulate.

3. Thermodynamic Relations: In the following treatment the standard notations for thermodynamic functions in classical equilibrium thermodynamics are retained. Thus,  $U$ ,  $H$ ,  $A$ ,  $G$ , and  $S$  will denote respectively the total energy, the enthalpy, the Helmholtz free energy, the Gibbs free energy, and the entropy.  $Q$  and  $W$  will represent heat and work supplied to the system. A superior dot will be used to denote the time derivative or rate.

$$\dot{U}(\text{system}) = \dot{Q} + \dot{W} \quad (4-1)$$

A distinction is drawn between monothermal and polythermal processes (and systems). A monothermal process is a process in which the entire system is in heat communication with a single heat reservoir of temperature  $T$  during the process. A polythermal process is a process in which the terminal parts of the system are separately in heat communication with heat reservoirs of temperature  $T_i$  during the process. Heat exchange between the surroundings and the parts on-the-line may be permissible but is not analyzed further in the present work. For a monothermal

process, then:

$$\dot{Q} = -\dot{T} \dot{S}(r) \quad (4-2)$$

where  $\dot{S}(r)$  denotes the rate of accumulation of entropy in the heat reservoir. Similarly, for a polythermal process

$$\dot{Q} = -\sum_i T_i \dot{S}_i(r) \quad (4-3)$$

When a steady exchange of mass between terminal parts of the system takes place, the parts on-the-line is point-wise invariant in time during the steady-flow process. Under such conditions one writes:

$$\dot{U}(\text{system}) = \sum_i U_i \dot{N}_i \quad (4-4)$$

where  $U_i$  represents the total energy per mole of the material in the  $i^{\text{th}}$  terminal parts of the system.

As an illustrative example the classical porous plug experiment is analyzed here by the present method (21). Fig. 1 depicts the classical Joule-Thomson experiment. A definite amount of gas and a plug constitute the system and are thermally insulated from the surroundings. The usual assumptions are made that the gas is flowing across the porous plug at a steady rate of  $\dot{N}$  moles per second, that the gradients in temperature and pressure can be localized in a region in the close vicinity of the porous plug, and, far from the plug, the thermodynamic state of the gas is characterized by the variables  $(T_+, P_+)$  and  $(T_-, P_-)$ . Under such conditions one writes:

$$\dot{U}(\text{system}) = \dot{W} = -P_+ \dot{V}_+ + P_- \dot{V}_- \quad (4-5)$$

Since the flow is between terminal parts and the part on-the-line is point-wise time invariant, one has:

$$\dot{U}(\text{system}) = \bar{U}_+ \dot{N}_+ + \bar{U}_- \dot{N}_- \quad (4-6)$$

where the superior bar indicates a molar property of the gas.  
the steady flow condition dictates:

$$-\dot{N}_+ = \dot{N}_- = \dot{N} \quad (4-7)$$

Hence one obtains

$$(\bar{U}_- - \bar{U}_+) \dot{N} = (P_+ \dot{V}_+ - P_- \dot{V}_-) \dot{N} \quad (4-8)$$

or

$$\bar{H}_- = \bar{H}_+ \quad (4-9)$$

where

$$\bar{H} = \bar{U} + P\bar{V}$$

In line with Equation (4-4) one can, in general, write

$$\dot{U}(\text{system}) = \sum_i U_i \dot{N}_i = -T\dot{S}^{(r)} + \dot{W} \quad (4-10)$$

$$\dot{H}(\text{system}) = \sum_i h_i \dot{N}_i = -T\dot{S}^{(r)} + \dot{W} + \sum_i P_i \dot{V}_i \quad (4-11)$$

$$\dot{A}(\text{system}) = \sum_i a_i \dot{N}_i = -T(\dot{S}^{(r)} + \sum_i s_i \dot{N}_i) + \dot{W} \quad (4-12)$$

$$\dot{G}(\text{system}) = \sum_i g_i \dot{N}_i = -T(\dot{S}^{(r)} + \sum_i s_i \dot{N}_i) + \dot{W} + \sum_i P_i \dot{V}_i \quad (4-13)$$

The rate of entropy production is given under steady flow conditions by:

$$\sigma = \dot{S}^{(r)} + \sum_i \dot{N}_i \bar{S}_i \quad (4-14)$$

In the following treatments it will be assumed that, for all the systems to be considered,  $\dot{W} + \sum_i P_i \dot{V}_i = 0$ , i.e., the only work involved is the PV work. Under such circumstances Equation (4-13) takes the form:

$$-\dot{G}(\text{system}) = T\sigma \quad (4-15)$$

4. **Migrational Equilibrium:** The conditions for a migrational equilibrium will now be sought. By migrational equilibrium one understands a steady state corresponding to a non-flow state with respect to a given chemical substance. When a steady migration of a given chemical substance into the  $K^{\text{th}}$  terminal part of the system takes place, one writes:

$$-\dot{G}(\dot{N}_K) = T\sigma(\dot{N}_K) \quad (4-16)$$

For the non-flow state with respect to the given chemical substance it follows that:

$$-\dot{G}(0) = T\sigma(0) \quad (4-17)$$

Combining Equations (16) and (17) one has:

$$-\Delta\dot{G} = T\Delta\sigma \quad (4-18)$$

where

$$\Delta \dot{Z} \equiv \dot{Z}(\dot{N}_k) - \dot{Z}(0)$$

Dividing both sides of Equation (4-18) by  $\dot{N}_k$  and passing to the limit of vanishing mass flow via a sequence of steady-flow states one writes:

$$-\lim_{\dot{N}_k \rightarrow 0} (\Delta \dot{G} / \dot{N}_k) = T \lim_{\dot{N}_k \rightarrow 0} (\Delta \sigma / \dot{N}_k) \quad (4-19)$$

Since this notion of limiting operation is a basic tool in the application of Tykodi's formalism, one wishes to employ a short-hand notation. One adopts the following notation:

$$\delta \dot{Z} / \tilde{\delta} \dot{N}_k = \lim_{\dot{N}_k \rightarrow 0} \left\{ \left[ \dot{Z}(\dot{N}_k) - \dot{Z}(0) \right] / \dot{N}_k \right\} \quad (4-20)$$

the limit being always approached via a sequence of steady-flow states. The fundamental postulate now takes the form:

$$\delta \sigma / \tilde{\delta} \dot{N}_k = 0 \quad (4-21)$$

Substituting Equation (4-21) into Equation (4-19) one obtains:

$$-\delta \dot{G} / \tilde{\delta} \dot{N}_k = -\sum_i \delta(\varepsilon_i \dot{N}_i) / \tilde{\delta} \dot{N}_k = 0 \quad (4-22)$$

For the case of a steady flux of mass between two terminal parts  $(\alpha, \beta)$  of a system, one has  $\dot{N}_\alpha + \dot{N}_\beta = 0$  and that Equation (4-22) reduces to:

$$\varepsilon_\alpha - \varepsilon_\beta = 0 \quad (4-23)$$

Equation (23) yields familiar results in equilibrium thermodynamics. For example, if and refer to gas phase and liquid

phase respectively, the condition for the monothermal gas-liquid equilibrium is just:

$$\mu_{\text{gas}} = \mu_{\text{liq}} \quad (4-24)$$

where  $\mu$  stands for the chemical potential, or the partial molar Gibb's free energy.

5. Migrational Equilibrium in a Monothermal Concentration Field: The problem of migrational equilibrium in a monothermal concentration field will now be analyzed. The situation is depicted in Fig. 2.

There are two fluid components 1 and 2 present in the spatial region marked MIX, which communicates with terminal parts A and B via membranes permeable to component 1 alone and with terminal parts  $\alpha$  and  $\beta$  via membranes permeable to component 2 exclusively. A steady flow of component 1 is induced through the MIX region, and the conditions for the migrational equilibrium of component 2 in the concentration field formed by the flow of component 1 are sought.

Now with respect to the fundamental postulate, the reference state of the system corresponds to the nonflow state of component 2 (with the flow of component 1 alone, or monoflow state). When a steady flux of component 2 is established through the MIX region with the pressures  $P_A$  and  $P_B$  kept fixed, one writes for the biflow state:

$$-\dot{G}(\dot{N}_A, \dot{N}_\alpha) = T (\dot{N}_A, \dot{N}_\alpha) \quad (4-25)$$



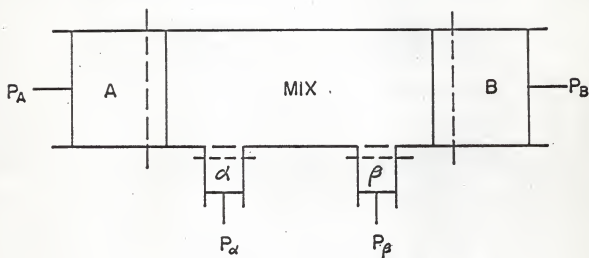


Fig.2. Migrational equilibrium in a mono-thermal concentration field.

At static condition, the partial molar Gibbs free energy of a chemical substance is identical to the chemical potential. When a substance is in motion, one adds the molar kinetic energy of macroscopic motion  $K$ , to the chemical potential to get the partial molar Gibbs free energy (21) and one writes:

$$g = \mu + K \quad (4-26)$$

An important property of the molar kinetic energy of macroscopic motion is obtained as follows. Allowing a bracketed subscript (i) to denote the property of component i and denoting the molecular weight and volumetric flow rate by  $M_{(i)}$  and  $V_{(i)}$  respectively and if the cross sectional area of the conduit perpendicular to the flow direction is denoted by  $A_s$  one has:

$$K_{(i)} = \frac{M_{(i)}}{2} \left( \frac{\dot{V}_{(i)}}{A_s} \right)^2$$

or

$$\begin{aligned} K_{(i)} &= \frac{M_{(i)}}{2} (\dot{N}_{(i)} \bar{V}_{(i)} / A_s)^2 \\ &= \frac{\dot{N}_{(i)}^2}{2} M_{(i)} \left( \frac{\bar{V}_{(i)}}{A_s} \right)^2 \end{aligned} \quad (4-27)$$

and

$$\dot{N}_{(i)} K_{(i)} = \dot{N}_{(i)}^3 \left( \frac{M_{(i)}}{2} \right) \left( \frac{\bar{V}_{(i)}}{A_s} \right)^2$$

Applying the limiting flow operation:

$$\begin{aligned} \delta \dot{N}_{(1)K(1)} / \tilde{\delta} \dot{N}_{(k)} &= 3N_{(1)}^2 \left(\frac{N}{2}\right) \left(\frac{V}{A_S}\right)^2 (\delta \dot{N}_{(1)} / \tilde{\delta} \dot{N}_{(k)}) \\ &= 3K_{(1)} (\delta \dot{N}_{(1)} / \tilde{\delta} \dot{N}_{(k)}) \end{aligned} \quad (4-28)$$

The left hand side of Equation (4-25) is, in a more explicit form,

$$\begin{aligned} &-(\varepsilon_A \dot{N}_A + \varepsilon_B \dot{N}_B + \varepsilon_\alpha \dot{N}_\alpha + \varepsilon_\beta \dot{N}_\beta) \\ &= -(\mu_A + K_A) \dot{N}_A + (\mu_B + K_B) \dot{N}_B + (\mu_\alpha + K_\alpha) \dot{N}_\alpha + (\mu_\beta + K_\beta) \dot{N}_\beta \end{aligned}$$

Because of the nature of the problem, the K terms for component 2 may be neglected. And one rewrites Equation (4-25) as:

$$-\left\{(\mu_A + K_A) \dot{N}_A + (\mu_B + K_B) \dot{N}_B + \mu_\alpha \dot{N}_\alpha + \mu_\beta \dot{N}_\beta\right\} = T\sigma \quad (4-29)$$

Now, noting that  $\dot{N}_A + \dot{N}_B = 0$  and  $\dot{N} + \dot{N} = 0$  and applying the limiting operation,  $\delta / \tilde{\delta} \dot{N}_\alpha$ , to Equation (4-29), and using Equation (4-28) one has:

$$-\left\{\left[(\mu_A + 3K_A) - (\mu_B + 3K_B)\right] (\delta \dot{N}_A / \tilde{\delta} \dot{N}_\alpha) + (\mu_\alpha - \mu_\beta)\right\} = T \frac{\delta \sigma}{\tilde{\delta} \dot{N}_\alpha} \quad (4-30)$$

The right hand side of Equation (30) vanishes according to the fundamental postulate. Hence, one has:

$$\mu_\alpha - \mu_\beta = -[R_{\alpha\beta}] (\varepsilon_A^* - \varepsilon_B^*) \quad (4-31)$$

where

$$g^* \equiv \mu + 3K \text{ and } [R_{\alpha\beta}] = \delta \dot{N}_\alpha / \delta \dot{N}_\beta$$

Identifying subscripts are attached to the  $[R]$  quantity to indicate the points in the concentration field between which chemical potential differences are being computed. If the flow of the two fluids is coupled, i.e.,  $[R_{\alpha\beta}] \neq 0$ , then the flow of component 1 sets up a gradient in the chemical potential of component 2. Here  $g^*$  behaves as a driving potential for the exchange of mass. The quantity  $g^* = \mu + 3K$  plays an important role in subsequent applications.

6. A Generalized Problem of Migrational Equilibrium: A situation as illustrated in Fig. 3 will be analyzed. Fig. 3 depicts a one-component fluid system consisting of two parallel streams of fluid (flowing through conduits of uniform bore) connected by a linkage through which a steady flux of fluid takes place. The system is divided up into terminal parts ( $x+$ ,  $x-$ ) with well defined fluid velocities under all conditions and parts on-the-line which are stationary under conditions of steady flow, including conditions of steady exchange of fluid between the tubes through the connecting linkage. For this situation, Equation (4-11) is substituted into Equation (4-13)

$$-\sum g_{xy} N_{xy} = T\sigma - \dot{W} - \sum p_{xy} \dot{V}_{xy} \quad x = \alpha, \beta, y = +, - \quad (4-33)$$

where  $g_{xy} = \mu_x + k_{xy}$  and  $\sigma$  represents the entropy production of the process.

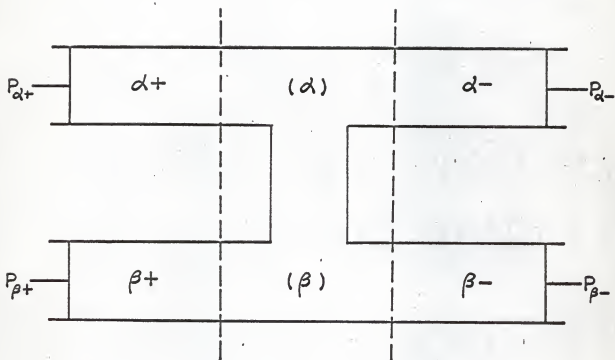


Fig.3. Analysis of a general problem in migrational equilibrium  $P_{x+} \geq P_{x-}$ ,  $x = \alpha, \beta$ .

In the presence of a steady flux of fluid through the connecting link, one writes:

$$\dot{N}_{x+} + \dot{N}_{x-} = \dot{V}_x, \quad \dot{V}_\alpha + \dot{V}_\beta = 0 \quad (4-34)$$

where  $\dot{V}_x$  represents the rate of influx of fluid into the x conduit via the connecting link. Equation (4-33) is now written in an expanded form:

$$-\left\{\mu_\alpha \dot{V}_\alpha + \mu_\beta \dot{V}_\beta + \sum \dot{N}_{xy} K_{xy} + \sum P_{xy} \dot{V}_{xy}\right\} = T\sigma \quad (4-35)$$

Applying the limiting operation,  $\delta/\delta\tilde{V}_\alpha$ , to Equation (37), and using the result of Equation (28) i.e.,  $\delta(\dot{N}_{x+} K_{x+} + \dot{N}_{x-} K_{x-})/\delta\tilde{V}_x = 3K_x$ , ( $K_x$  being considered as the average value of  $K_{x+}$  and  $K_{x-}$ )

$$\varepsilon_\alpha^* - [D_\alpha] = \varepsilon_\beta^* - [D_\beta], \quad (4-36)$$

where  $\varepsilon_x^* = \mu_x + 3K_x$  and  $[D_x] = -\delta(\sum P_{xy} \dot{V}_{xy})/\delta\tilde{V}_\alpha$ . Equation (36) is the final result of the preceeding analysis. It has a far reaching significance in the analysis of migrational equilibrium in general. The  $[D]$  term may be named as "dissipation function" and physically represents the dissipating effect, i.e., the viscous dissipation.

Now, one wishes to explore the implications of Equation (36) on the problem of phase equilibrium in the most general situation, i.e., the various phases in contact are allowed to move with different velocities. One considers the distributions of a certain chemical substance between two phases which are in relative motion.

Fig. 4 shows the migrational equilibrium (or equilibrium distribution) of a substance between two phases in relative motions. Since the interphase of the two phases, as pictured in Fig. 4, may be thought of as an "extended" connecting link (referring to Fig. 3), one expects that the equilibrium distribution will be governed by Equation (36):

$$g_{\alpha}^{*} - [D_{\alpha}] = g_{\beta}^{*} - [D_{\beta}] \quad (4-36)$$

If one is allowed to neglect the dissipative term  $D$ , one has:

$$g_{\alpha}^{*} = g_{\beta}^{*} \quad (4-37)$$

for the condition of migrational equilibrium.

When one may further neglect the kinetic effect of macroscopic motion,  $K$ , the familiar relationship established by the classical equilibrium thermodynamics results:

$$\mu_{\alpha} = \mu_{\beta} \quad (4-38)$$

In the following sections use will be made of the preceeding results in analyzing two simplifying limiting cases.

7. Corrections for Manometer Readings: The problem of measuring gas flow by use of the mercury manometer will be analyzed. Under the steady flow condition the gas in the manometer arm will be in migrational equilibrium with the gas flowing in the conduit. Application of Equation (37) in this situation leads to:

$$\mu + K = \mu_{\text{man}} \quad (4-39)$$

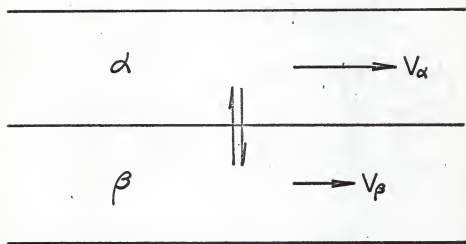


Fig. 4. Distribution of a chemical substance between two phases.



where unsubscripted symbols represent the mainstream properties. When the state of the gas may be described by the ideal gas law, one has (22):

$$\mu = \mu^0 + RT \ln P \quad (4-40)$$

and  $K = \frac{Mv^2}{2}$ , where M and v represent the molecular weight and linear velocity of the gas, Equation (41) yields:

$$P/P_{\text{man}} = \exp (-3Mv^2/2RT) \quad (4-41)$$

To examine the consequence by way of numerical computation one considers the case of air flowing with a velocity of 100m/sec at 0°C. Using M = 29 for air:

$$\begin{aligned} \frac{3Mv^2}{2RT} &= \frac{3 \times 29 \times (10,000)^2}{2 \times 82.06 \times 1033 \times 960 \times 273} \\ &= 0.1924 \end{aligned}$$

and consequently

$$\begin{aligned} P/P_{\text{man}} &= e^{-0.1924} \\ &= 0.825 \end{aligned}$$

In the preceeding analysis one neglects the dissipative effect [D], and thus obtains a somewhat exaggerated result. However, this example may serve to bring out the effect of the kinetic term of macroscopic motion when the gas is flowing with a velocity of the order of 100m/sec.

8. Mass Transfer Processes: In the usual air liquification process, compressed air is passed through packed bed dryers (usually silica or aluminum gels and more recently molecular sieves) prior to entering the refrigeration unit. The velocity of air is usually high enough to justify consideration of the kinetic term  $K$ . One is led to suspect that the equilibrium moisture content of the flowing air would be lower than if the air is in static contact with the adsorbent. One pictures the situation by means of a model in which the adsorbent is surrounded by a thin stagnant film of air beyond which the bulk of air is flowing. Neglecting the dissipative effect one applies Equation (4-37) to this situation:

$$\mu + 3K = \mu_s \quad (4-44)$$

where the unsubscripted symbols represent the mainstream and the subscript  $s$  refers to the stagnant air film. Under such conditions water vapor is not expected to obey the ideal gas behavior, and one writes (22):

$$\mu = \mu^0 + RT \ln f \quad (4-45)$$

where  $\mu^0$  depends on the temperature alone, and  $f$  denotes the fugacity.

Substituting of Equation (4-45) into Equation (4-44) leads to

$$RT \ln \frac{f}{f_s} = -3K = -\frac{3Mv^2}{2} \quad (4-46)$$

or

$$\frac{f}{f_s} = \exp \left( - \frac{3Mv^2}{2RT} \right)$$

$f_s$  is the saturation fugacity of water vapor in static condition.

In leaching processes, solvent flows past stationary beds of solid material. Utilizing the similar model as in the preceding example, one envisages a stagnant solvent film surrounding the solid particle. For this situation one writes (22):

$$\mu = \mu^* + RT \ln \gamma x$$

where  $\mu^*$  is a function of temperature and pressure, and  $x$  and  $\gamma$  stand for the mole fraction and activity coefficients of the solute. Carrying through similar manipulations, one obtains:

$$\frac{\gamma x}{\gamma_s x_s} = \exp \left( - \frac{3Mv^2}{2RT} \right) \quad (4-47)$$

The results of the preceding analysis point to a reconsideration of the so-called "driving force" in mass transfer. In the conventional design approach to the design of mass transfer processes between two phases, concentration (or partial pressure) difference in the two phases accounts for the driving force. The equilibrium concentrations and partial pressures are traditionally evaluated at static conditions, (i.e., when there is no relative motion between the phases). Equations (4-46) and (4-47) point to a need for correction on the values of equilibrium concentration when relative motion between the phases is

significant. It is desirable to draw a distinction between steady state concentration (or partial pressure) and static equilibrium concentration (or partial pressure) and the former should be used whenever relative motion between different phases is of considerable significance.

9. Summary: Tykodi's theory has been successfully applied in the analysis of migrational equilibrium. However, it must be emphasized that the legitimacy of Tykodi's theory rests upon a postulate which is yet to be proven. Moreover, in order to apply the fundamental postulate in the form of the limiting operator  $\frac{\delta}{\delta n_k}$  it is essential that one non-flow state with respect to a certain chemical substance must be identifiable. This requirement imposes a practical limitation upon the domain of applicability of Tykodi's formalism.

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## NOMENCLATURE

A	= Helmholtz free energy
$A_s$	= cross sectional area
a	= generalized thermodynamic function (Chapter 1), molar Helmholtz free energy (Chapter 4)
B	= magnetic induction
c	= concentration
D	= dissipation function
$D_{i,j}$	= Fick's law diffusional coefficient
f	= fugacity
G	= Gibbs free energy
g	= molar Gibbs free energy
H	= enthalpy
h	= molar enthalpy
$J_i$	= flux of component i
K	= kinetic energy of macroscopic motion
$L_{i,j}$	= constant
M	= molecular weight
$\dot{N}$	= molar rate of flow
P	= pressure
Q	= heat supplied to a system
R	= gas constant
S	= entropy
s	= molar entropy
T	= temperature



- $U$  = wave function (Chapter 1), mean velocity (Chapter 3),  
 total energy (Chapter 4)  
 $u$  = molar total energy  
 $\dot{V}$  = volume rate of flow  
 $\bar{V}$  = mean molar volume  
 $v$  = linear velocity  
 $W$  = work done on the system  
 $x_i$  = generalized thermodynamic force  
 $\gamma$  = activity coefficient  
 $\mu$  = chemical potential  
 $\Omega_{ij}$  = fundamental diffusional coefficient  
 $\omega$  = angular velocity

#### Subscript

- $C$  = cell fixed frame of reference  
 $O$  = solvent fixed frame of reference  
 $V$  = volume centered frame of reference  
 $M$  = mass centered frame of reference  
 $i, j$  = components

THE APPLICATION OF  
NONEQUILIBRIUM THERMODYNAMICS

by

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## ABSTRACT

This work consists of four chapters. In the first chapter, the context and scope of nonequilibrium thermodynamics are outlined. Critical considerations are given to the criteria of irreversibility. A brief historical development of the subject is sketched. Onsager's theory and associated problems are presented from a practical point of view. The second chapter is concerned with a controversial problem on the application of Onsager's reciprocal relations. It is emphasized that a legitimate choice of the conjugated forces and fluxes depends upon a more fundamental criterion than the notion of invariance of entropy production. Chapter three deals with isothermal multicomponent diffusion. The classical Fick's law of diffusion is compared with a formulation based on the scheme of nonequilibrium thermodynamics. The system  $\text{NaCl} - \text{KCl} - \text{H}_2\text{O}$  is investigated. While numerical computations based on existing data yield favorable results for Onsager's reciprocal relations, a vital defect in the formulation based on the scheme of nonequilibrium thermodynamics is revealed. In the final chapter, a new approach developed by R. J. Tykodi is presented. In treating nonequilibrium phenomena, Tykodi's method aims at preserving the phenomenological spirit characteristic of classical equilibrium thermodynamics. Problems of migrational equilibrium are successfully attacked by Tykodi's method.